Funded by the European Union
cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY
4TH GENERAL MEETING OF COST ACTION CA21101 "COSY"
COSY COST ACTION
MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES
CSIC

Structural and NMR properties of ionic liquid materials: insights from MD/QM modelling

Kęstutis Aidas[1], Žyginta Murnikova[1], Einaras Sipavičius[1], Dovilė Lengvinaitė[1]

[1]*Institute of Chemical Physics, Faculty of Physics, Vilnius University, Saulėtekio ave. 3, LT-10257 Vilnius, Lithuania*
kestutis.aidas@ff.vu.lt

Molecular dynamics (MD) simulations combined with the quantum mechanics/molecular mechanics (QM/MM) models have proven to be a powerful computational technique for accurate predictions of electronic properties of extensive molecular systems. In this presentation we will discuss our recent successes in describing the structural and nuclear magnetic resonance (NMR) properties of ionic liquid (IL) systems using the integrated MD-QM/MM scheme based on classical MD simulations and density functional theory.

Relative ^{1}H NMR spectra of the [C$_4$mim][BF$_4$] IL and its aqueous mixtures were recently computed with the overall root-mean-square deviation of 0.2 ppm.[a] Even the previously troublesome chemical shift of the proton at position 2 in the imidazolium ring was also predicted very accurately.

Scrutinizing intermolecular organization in aqueous mixtures of [Cho][Lys] IL, the analysis of MD trajectories revealed the formation of highly polar and less polar domains in IL-rich mixtures.[b] Isolated water pockets were found to be situated at the interface of the polar and nonpolar ionic domains. The experimentally observed upfield shift of the NMR signal of protons in fast exchange with the rising content of the IL was successfully rationalized.

We have used the MD-QM/MM computational scheme to study the molecular mechanism behind the increased solubility of antidiabetic drug molecule glibenclamide in aqueous solution of [Cho][Trp] IL.[c] Classical MD simulations indicate prolific interactions between the constituent ions of the IL and glibenclamide, and thus these ions are screening the hydrophobic drug molecule from the polar water molecules.

Very recent computational results regarding the structural and NMR properties of a model tetrapeptide Ala-Glu-Pro-Phe in aqueous mixtures of [C$_2$mim][TFA] IL will be presented as well.

References:

[a] Sipavičius, E.; Majauskaitė, G.; Lengvinaitė, D.; Bielskutė, S.; Klimavicius, V.; Mocci, F.; Laaksonen, A.; Aidas, K. Towards accurate modelling of ^{1}H NMR spectra of ionic liquids: The case of [C$_4$mim][BF$_4$] and its aqueous mixtures. Chem. Phys. Lett., 2025, 877, 142295. https://doi.org/10.1016/j.cplett.2025.142295

[b] Sipavičius, E.; Mikalauskas, L.; Klimavicius, V.; Aidas, K. Intermolecular organization in aqueous mixtures of choline lysinate studied via NMR and molecular dynamics/quantum mechanics. Phys. Chem. Phys. Chem. Phys., 2025, 27, 14790-14803. https://doi.org/10.1039/D5CP00861A

[c] Murnikova, Ž.; Klimavicius, V.; Mocci, F.; Laaksonen, A.; Aidas, K. On the mechanism behind the enhanced solubility of glibenclamide in aqueous ionic liquid solution. J. Mol. Liq., 2025, 422, 127153. https://doi.org/10.1016/j.molliq.2025.127153